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Thermogravimetry: a means of estimating the relative fertility of the mineral soils of Barbados

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Abstract

Thirty seven soil types from Barbados were analyzed using thermogravimetry (TG) over the temperature range 50–1000°C to determine the associated weight loss. The relative thermal activity "*F*" of each soil sample correlated significantly with cation exchange capacity (CEC) and clay-related exchange capacity (correlation coefficients ranged from 0.44 to 0.70). The CEC was found to relate to the relative thermal activity through the relationship: $F = 1.94 + (0.032\ \text{CEC})$. On the basis of TG, intra-specific variations within soil associations was found to be as significant as inter-specific variations with some of the least as well as the most fertile soils being found among the St. Philip Plain and Grey brown associations. Sugar cane yield per acre for seven consecutive years starting in 1993 was also found to correlate significantly with thermal activity resulting in a linear correlation coefficient of 0.80. On the basis of the above findings "*F*" is being recommended for determination of the relative fertility levels of the mineral soils of Barbados.

Keywords: Thermogravimetry; Cation exchange capacity; Soil association; Soil group

1. Introduction

Soils of Barbados were developed over either coralline limestone or, in places where the coral cap has been eroded, over Eocene sediments and radiolarian chalk [1]. Of the many theories which were advanced in support of the emergence of the island, Broecker et al. [2] who used radiochemical dating to determine the age of minerals present in the soil, offered the most creditable explanation when they stated that gradual emergence of the coral terraces at a constant rate over the past 125,000 years was the most likely mode of formation of the island.

The findings by Broecker et al. [2] in many ways supported earlier claims that soil age and fertility were inextricably linked and that fertility status of these soils decreased from high to low elevations [3–6]. The logical deduction therefore was that the red soils found at elevations between 215–305 m above sea level were the most mature followed by the intermediate red and grey which were found at heights of 120–215 m and 60–120 m, respectively. Soils of the black association occurring at elevations of 1–60 m were considered to be the least mature of all the soil types of Barbados.

During the mid sixties the soils of Barbados were mapped and classified based on pedogenic, topographic and drainage characteristics and color, texture

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and chemical properties to a lesser extent [7]. They were able to describe ten major soil associations which were further subdivided into groups on the basis of the soil depth. Soils developed over the limestone were described as calcareous and include the Red brown, Yellow brown and St. John's Valley associations which are similar to Ustalfs of the Alfisol Order and the grey brown, Black, St. George's Valley, St. Philip Plain, and Coastal associations which all resemble the Usterts of the Vertisol Order [8]. Soils developed over radiolarian chalks and Eocene sediments are represented by Red sands and Scotland District sandstones.

Over the past three centuries monoculture was practised in Barbados with sugarcane being the only crop of economic importance. Fertilizer applications were restricted to the use of nitrogen and potassium since, according to Elwin [9], there was no response to phosphorus application. This apparent lack of response to phosphorus was verified by Ahmad [10] who explained that the phenomenon was due basically to the abundance of easily available phosphorus.

Fertilizer regimes have changed over the pass four decades from application of different quantities to the various soil associations to the present regime where all soil types are treated with similar quantities of fertilizer [11]. This system of fetilization is not the most resourceful since soils require fertilizer based on their inherent fertility status.

Thermogravimetry (TG) is limited to those reactions taking place in the soil with accompanying loss in weight, and so is mainly used in conjunction with DTA and DSC techniques which are more common [12–14]. Since soil constituents associated with fertility are all thermally active within the experimental temperature range of 50–1000°C, therefore, loss of weight on heating should reveal the relative contributions of each component. Such reactions include evaporation of soil moisture, combustion of organic matter and dehydroxylation of clays [15].

During this study an effort was made to use TG data from 37 soil samples representing the major soil types of Barbados to determine their relationship with cation exchange capacity (CEC) of the respective soils and sugarcane yields associated with the respective soils. An effort was made to verify whether there is significant intra-specific variation in fertility levels of each of the ten major associations.

2. Experimental

Soil group identification was based on the scheme outlined by Vernon and Carroll [7] and the accompanying soil map of Barbados. Soil sampling was restricted to the top 30 cm and 30 randomly selected soil cores (3 cm diameter and 30 cm long) were mixed and homogenized before processing. Soil horizons represented at this depth have been described by Gibbs et al. [16] in accordance with USDA [8].

Soil samples were prepared according to Oswald and Wiedermann [17] and Schwenker [18] and 30–75 mg of each subjected to heat treatment in a temperature range of 50–1000°C using a Du Pont 910 DSC Thermal Analyzer. The instrument settings were: time base of 2.5; T zero shift; T range: 50; Y range: 20; Y′ range: 10; and Y-axis: T. Analar calcium oxalate monohydrate ($CaC_2O_4{\cdot}H_2O$) (BDH, UK) was used to standardize the instrument.

Chemical analyses including percent carbonate, organic carbon and total nitrogen, and total exchangeable base, CEC, exchangeable calcium, magnesium, potassium and sodium are described [19].

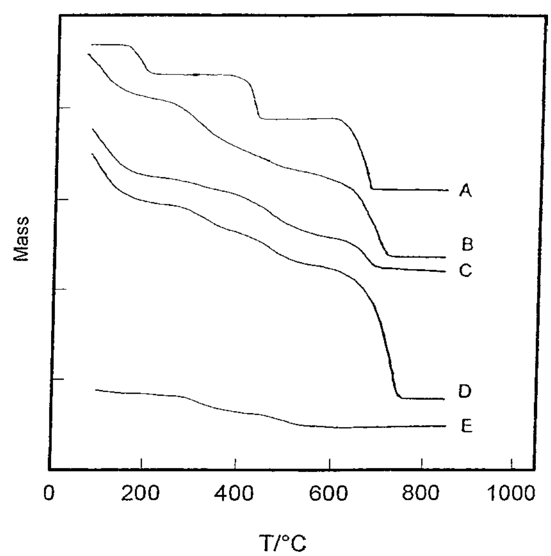

Fig. 1. Thermogravimetric patterns of calcium oxalate monohydrate and four soil samples representing different soil types obtained using the Du Pont 910 DSC Thermal Analyzer. Curves specifically represent; A: calcium oxalate monohydrate; B: 174-Alluvial; C: Red brown (dark variant); D: 71-Red sands (dark variant); E: 173-Scotland sandstone.

Clay content of soil samples was done by mechanical analysis using the hydrometer method [20]. Mineralogical composition of clay extracts was determined using X-ray diffraction analysis on clay samples prepared after the method outlined by Rich [21].

Crop yield data for sugarcane grown on the respective soil types over a three year period including 1997, 1998 and 1999 were obtained from the local cane breeding and variety testing station-sugar technology research unit (STRU). The possibility that soil thermal properties may influence chemical properties and crop yields were investigated. In this investigation a relationship was sought between the numerical values of each soil chemical factor and the relative heat loss associated with all soil components except carbonates

Table 1
Thermogravimetric weight loss, relative thermal activity (*F*)[a,b] and average sugarcane yields over 3 consecutive years harvest for 37 Barbadian soil types

Soil association	Wt. loss (%)	(*F*)[b]	CEC (meq/100 g)	Sugar yield (tonnes/acre)
10-St. Philip Plain	7.39	1.08	93.39	2.39
12b-St. Philip Plain	38.81	5.67	–	3.25
13-St. Philip Plain	29.94	4.38	–	2.85
20-St. George Valley	38.81	5.67	70.22	3.17
30-Black (normal)	39.18	5.73	–	3.14
32-Black (shallow)	41.95	6.13	–	3.87
40-Grey brown (normal)	17.56	2.57	59.20	3.11
41-Grey brown (normal)	28.27	4.13	66.01	2.74
41/40-Grey brown (normal)	45.46	6.65	68.29	3.96
42/40-Grey brown (normal)	23.10	3.38	58.37	2.05
42-Grey brown	15.01	2.19	53.47	1.97
42-Grey brown (shallow)	12.38	1.81	53.12	2.17
47-Grey brown (sandy)	15.52	2.27	34.80	–
48-Grey brown (leeward)	35.85	5.24	58.03	2.63
50-Yellow brown	40.29	5.89	46.64	3.48
54-Yellow brown	36.78	5.38	44.09	3.70
60-Red brown (normal)	35.67	5.21	22.72	3.37
61-Red brown (shallow)	21.99	3.21	25.09	2.91
64-St. John Valley	26.98	3.94	23.43	3.62
65-St. John Valley	43.72	6.39	21.90	3.92
70-Red sand	7.39	1.08	36.07	1.57
71-Red sand (dark)	28.46	4.16	43.31	2.42
80-Coastal (normal)	40.29	5.89	88.13	–
81-Coastal (association)	31.79	4.65	79.06	–
81-Coastal (shallow)	24.21	3.54	77.18	–
84-Coastal (leeward)	24.58	3.59	54.86	–
86-Coastal (south coast)	38.07	5.57	88.13	–
103-Grey brown (oceanic)	9.61	1.40	64.87	2.34
110-Red brown (oceanic)	31.42	4.59	17.09	–
115-Bissex Hill (oceanic)	30.68	4.49	13.73	–
122-Joe's River Mud	20.33	2.97	15.01	–
131-Scotland sandstone	6.84	1.00	7.49	–
141-Alluvial	25.50	3.73	15.55	–
171-Alluvial	17.93	2.62	10.27	–
172-Alluvial	18.66	2.73	14.37	–
173-Scotland sandstone	8.69	1.27	4.93	–
174-Alluvial	29.20	4.27	14.59	–

[a] (–) Indicates data not available.
[b] Relative thermal activity (*F*) derived from adjusting percent weight loss relative to the lowest weight decrease which was assigned a value of 1.

by performing linear correlation analysis using the Mini Tab microcomputer program (Making Data Analysis Easier).

3. Results and discussion

Cation exchange capacity (CEC) being the single most important indicator of soil fertility [20,21], was used in the correlation with thermogravimetric data associated with thermal activities of all soil constituents except carbonate. Contributions to thermal weight loss did not include those made by carbonate since it is assumed that clay-sized carbonates, found in the soils of Barbados, only influence the physical rather than chemical properties of soils [22]. Carbonate contributions to weight loss of soils are recognized as the final weight change occurring around

Table 2
Chemical properties of 37 soil types taken from among the 10 soil associations of Barbados[a]

Soil association	Percent				Exchangeable ions (meq/100 g)			
	Clay	OC	N	CO_3^{2-}	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}
10-St. Philip Plain	44.9	1.96	0.18	20.3	56.3	1.94	0.53	1.46
12b-St. Philip Plain	62.6	1.00	0.16	4.70	39.9	0.99	1.43	1.17
13-St. Philip Plain	50.6	0.96	0.21	4.05	33.5	6.94	1.44	0.72
20-St. George Valley	61.6	1.27	0.17	4.90	37.7	4.71	1.14	0.63
30-Black (normal)	66.3	3.88	0.30	6.14	89.1	1.56	0.27	0.82
32-Black (shallow)	69.2	1.62	0.40	4.70	38.5	0.45	1.62	0.65
40-Grey brown (normal)	51.9	3.00	0.31	15.4	60.4	2.11	0.54	0.58
41-Grey brown (normal)	57.9	1.66	0.14	10.4	70.3	2.28	0.38	0.65
41/40-Grey brown (normal)	59.9	1.80	0.11	9.21	57.3	1.27	0.60	2.35
42/40-Grey brown (normal)	51.2	2.04	0.66	11.9	37.5	2.11	1.35	2.36
42-Grey brown	46.9	1.56	0.25	14.0	39.5	6.46	0.51	0.55
42-Grey brown (shallow)	46.6	2.44	0.15	6.77	50.0	2.71	1.31	3.18
47-Grey brown (sandy)	31.4	1.67	0.33	2.93	26.7	0.67	1.34	0.84
48-Grey brown (leeward)	50.9	0.88	0.33	1.64	12.1	0.39	3.23	1.17
50-Yellow brown	67.6	1.23	0.20	1.75	56.6	4.27	0.45	0.62
54-Yellow brown	63.9	2.51	0.44	5.61	67.5	1.33	0.42	1.24
60-Red brown (normal)	23.4	1.56	0.29	1.92	4.88	0.31	0.86	0.56
61-Red brown (shallow)	69.7	0.61	0.18	2.93	13.7	0.14	0.69	1.68
64-St. John Valley	68.9	2.07	0.32	2.96	53.4	0.44	0.45	0.81
65-St. John Valley	64.4	2.42	0.24	1.99	64.6	0.50	0.27	1.92
70-Red sand	33.4	0.33	0.21	0.75	9.31	0.70	1.02	0.77
71-Red sand (dark)	40.1	1.75	0.27	18.6	32.1	2.85	2.33	0.55
80-Coastal (normal)	61.2	1.01	0.22	2.04	24.7	3.78	3.86	1.54
81-Coastal (association)	54.9	1.17	0.18	7.39	50.6	4.32	3.98	4.42
81-Coastal (shallow)	53.6	0.55	0.09	2.27	39.5	6.46	1.18	0.74
84-Coastal (leeward)	38.1	1.22	0.28	10.7	28.8	7.32	1.30	0.64
86-Coastal (south coast)	61.2	1.58	0.17	6.33	48.5	2.71	3.39	0.34
103-Grey brown (oceanic)	56.9	2.27	0.18	32.8	44.6	1.50	0.41	2.66
110-Red brown (oceanic)	53.4	2.82	0.37	11.6	18.6	0.61	0.86	1.35
115-Bissex Hill (oceanic)	42.9	2.38	0.26	8.56	18.6	1.26	1.09	1.93
122-Joe's River Mud	46 9	2.03	0.10	–	8.65	0.60	0.83	1.04
131-Scotland sandstone	6.84	1.43	0.10	–	1.51	0.30	0.55	0.52
141-Alluvial	48.6	2.05	0.22	–	1.89	0.34	4.70	2.66
171-Alluvial	32.1	1.09	0.18	1.34	31.4	5.83	1.58	9.02
172-Alluvial	44.9	1.25	0.22	1.94	20.9	0.28	1.14	0.63
173-Scotland sandstone	15.4	1.98	0.11	–	0.94	0.36	1.11	0.52
174-Alluvial	45.6	1.84	0.28	10.8	34.3	3.94	3.44	0.99

[a] (–) Indicates no carbonate present.

760–810°C thus making it rather easy to distinguish and eliminate (Fig. 1).

Percent weight loss associated with the thermogravimetric curves were adjusted relative to each soil and referred to as "relative thermal fertility" (F). Relative thermal fertility is derived from adjusting percent loss relative to the lowest weight decrease which was obtained for the soil sample designated 131-Scotland sandstone and assigned an "F" value of 1. For the purpose of the statistical analyses soils were designated calcareous or noncalcareous on the basis of their carbonate content which limited the former to carbonate levels above 5.0%. Chemical properties for all soil samples are given in Tables 1 and 2. Linear correlation coefficients of 0.59, 0.60 and 0.44 were obtained for linear comparisons of CEC with "F" for all soils (37 soil samples), the noncalcareous group (18 soil samples) and the calcareous group (19 soil samples) respectively, and all coefficients were significant ($P < 0.01$). This finding suggests that carbonate content of soils impacts negatively on chemical exchangeability of soils, and that crude weight loss associated with clay, silt and organic matter is a significant measure of fertility of soils.

Thermal fertility of soils as is derived from TG analysis confirms that Barbadian soil groups including the 173- and 131-Scotland sandstone, 70-Red sands, 10-St. Philip Plain and the 103-Grey brown (Oceanic) are among the least fertile soils whereas the 65-St. John Valley and 41/40-Grey brown associations are among the most fertile (Fig. 2). The extent of the intra-association variation among soil groups is due largely

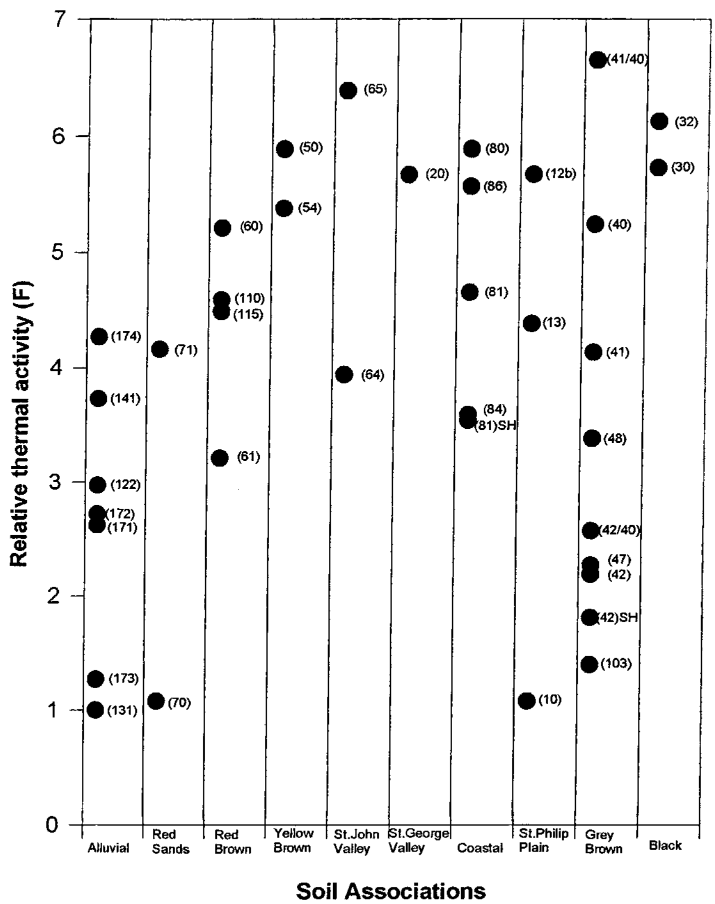

Fig. 2. Relative thermal activity (F) for 37 soil types representing the 10 major soil associations of soils in Barbados. SH: indicates shallow topsoil in soil associations, (81)SH and (42)SH.

to their clay content. This finding confirms that the level of intra-specific variation in soil fertility is in many instances greater than interspecific association variations which were not previously mentioned. It also refutes researchers claims that fertility status of soil types of Barbados is association specific in that all Red soils are more fertile than the Black soils.

Soil organic matter content of Barbadian soil types is less than 4.0%, Gibbs [19], whereas clay content of the vast majority of these soil types was greater than 50%. A linear regression coefficient of 0.25 for CEC with percent organic matter, non-significant ($P < 0.05$), implies that exchange capacity of these soils is due basically to the type and amount of clay present. It is on this basis that the product of percent clay content and the relative exchange capacity of the respective minerals constituting these clays-kaolinite and montmorillonite, were used as a measure of exchange capacity of the various soil types assessed during this study. Linear regression analysis of the numerical value of the above product with "F" gave a coefficient of 0.70 which is significant ($P < 0.05$). The correlation coefficient for linear regression analysis of "F" with sugarcane yield for seven consecutive years was found to be 0.80 which is significant ($P < 0.05$).

The current method of determining fertility levels of these soils is tedious and time consuming yet it offers no superior results to those obtained using thermal analysis. Based on data derived from TG analysis of the 37 soil samples assessed in this study, it was found that thermal and chemical expressions for exchange capacity are related through the equation: $F = 1.94 + (0.032\ \text{CEC})$.

4. Conclusions

Results for TG of soil samples examined in this study indicate that the relative thermal activity "F" can be employed as an easy and efficient method of determining relative fertility of the soil types of Barbados. Justification for use of this method as a measure of relative soil fertility is based on the significant correlations for TG-derived data and CEC, clay-related exchange capacity and sugarcane yield over a seven-year period. This method allows also for easy recognition of the intra- and inter-specific variation inherent in the ten soil associations of Barbadian soil types.

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